Chem 1515.001 - 006
Problem Set #6
Spring 2002

Name______________________________________

TA's Name __________________________________

Sec _____

ALL work must be shown to receive full credit. **Due in lecture at 8:30 a.m. on Monday, March 4, 2002.**

PS6.1. Calculate the vapor pressure for each of the following solutions at 25 ˚C;

a) 25.0 g of sucrose, $C_{12}H_{22}O_{11}$ dissolved in 250 g of water.

$$\mathbf{P_{soln} = \chi_{solvent} P^{\circ}_{H_2O}}$$

$$\mathbf{25.0\ gm\ C_{12}H_{22}O_{11}\left(\frac{1\ mole}{342.0\ gm}\right) = 0.0731\ mol}$$

$$\mathbf{250\ gm\ H_2O\left(\frac{1\ mol}{18.0\ gm}\right) = 13.9\ mol\ H_2O}$$

$$\mathbf{\chi_{solvent} = \frac{13.9\ mol}{13.9\ mol + 0.0731\ mol} = 0.995}$$

$$\mathbf{P_{soln} = 0.995\ (23.76\ mm) = 23.6\ mm\ of\ Hg}$$

b) 3.2 g of Na_2CO_3 dissolved in 400 g of water.

$$\mathbf{3.2\ g\ Na_2CO_3\left(\frac{1\ mol}{106\ g}\right) = 0.0302\ mol}$$

$$\mathbf{400\ g\ of\ water\left(\frac{1\ mol}{18\ g}\right) = 22.2\ mol}$$

$$\mathbf{Na_2CO_3}(aq) \rightarrow \mathbf{2Na^+}(aq) + \mathbf{2CO_3^{2-}}(aq)$$

$$\mathbf{0.0302\ mol\ Na_2CO_3\left(\frac{3\ mol\ particles}{1\ mol\ Na_2CO_3}\right) = 0.0906\ mol}$$

$$\mathbf{\chi_{H_2O} = \frac{22.2mol}{(22.2\ mol + 0.0906\ mol)}}$$

$$\mathbf{\chi_{H_2O} = 0.966}$$

$$\mathbf{P_{soln} = 0.966\ (23.76\ mm) = 22.9\ mm\ of\ Hg}$$

c) The vapor pressure of pentane and hexane at 25 ˚C are 511 mmHg and 150 mmHg respectively. Assuming ideal behavior determine the total vapor pressure above a solution prepared by mixing 45.0 mL of pentane (density = 0.63 $\frac{g}{mL}$) with 85.0 mL hexane (density = 0.66 $\frac{g}{mL}$).

$$\mathbf{45.0\ mL\ pentane\left(\frac{0.63\ g}{1\ mL}\right) = 28.4\ g}$$

$$\mathbf{85.0\ mL\ hexane\left(\frac{0.66\ g}{1\ mL}\right) = 56.1\ g}$$

$$\mathbf{28.4\ g\ pentane\left(\frac{1\ mole}{72.0\ gm}\right) = 0.394\ mol}$$

$$\mathbf{56.1\ g\ hexane\left(\frac{1\ mole}{86.0\ gm}\right) = 0.652\ mol}$$

PS5.1. (Continued)

$$\chi_{\mathbf{hexane}} = \frac{\mathbf{0.652\ mol}}{\mathbf{(0.652\ mol + 0.394\ mol)}}$$

$$\chi_{\mathbf{hexane}} = \mathbf{0.624} \qquad \chi_{\mathbf{heptane}} = \mathbf{0.376}$$

$$\mathbf{P_{soln}} = \chi_{\mathbf{pentane}}\mathbf{P^{\circ}_{pentane}} + \chi_{\mathbf{hexane}}\ \mathbf{P^{\circ}_{hexane}}$$

$$\mathbf{P_{soln}} = \mathbf{0.376 \cdot 511\ mmHg + 0.624 \cdot 150\ mmHg = 286\ mmHg}$$

PS6.2. To what temperature (˚C) would a solution containing 18.5 g of urea, $(NH_2)_2CO$, in 300. g of water have to be heated to have a vapor pressure of 89.5 mmHg?

$$\mathbf{P_{soln}} = \chi_{\mathbf{solvent}}\mathbf{P^{\circ}_{H_2O}}$$

$$\mathbf{18.5\ g\ (NH_2)_2CO}\left(\frac{\mathbf{1\ mol}}{\mathbf{60.0\ g}}\right) = \mathbf{0.308\ mol}$$

$$\mathbf{300\ gm\ H_2O}\left(\frac{\mathbf{1\ mol}}{\mathbf{18.0\ gm}}\right) = \mathbf{16.7\ mol\ H_2O}$$

$$\chi_{\mathbf{solvent}} = \frac{\mathbf{16.7\ mol}}{\mathbf{16.7\ mol + 0.308\ mol}} = \mathbf{0.982}$$

$$\mathbf{89.5\ mmHg} = \mathbf{0.982\ P^{\circ}_{H_2O}}$$

$$\mathbf{91.1\ mmHg} = \mathbf{P_{H_2O}}$$ **the temperature which water has a vapor pressure of 123 mmHg is 50 ˚C.**

PS6.3. Determine the freezing point and the boiling point of the solution in PS6.2.

$$\mathbf{molality} = \frac{\mathbf{0.\ 308\ mol\ (NH_2)_2CO}}{\mathbf{0.300\ kg\ H_2O}} = \mathbf{1.03\ molal}$$

$$\mathbf{\Delta T_{fp}} = \mathbf{mK_f}$$

$$= \mathbf{1.03\ molal}\left(\mathbf{1.86}\frac{\mathbf{^{\circ}C}}{\mathbf{m}}\right)$$

$$\mathbf{\Delta T_{fp}} = \mathbf{1.91\ ^{\circ}C}$$

$$\mathbf{T_{fp}} = \mathbf{-1.91\ ^{\circ}C}$$

$$\mathbf{\Delta T_{bp}} = \mathbf{mK_b}$$

$$= \mathbf{1.03\ molal}\left(\mathbf{0.512}\frac{\mathbf{^{\circ}\ C}}{\mathbf{molal}}\right)$$

$$\mathbf{\Delta T_{bp}} = \mathbf{0.527\ ^{\circ}C}$$

$$\mathbf{T_{bp}} = \mathbf{100.527\ ^{\circ}C}$$

PS6.4. What is the boiling point of an 12.5% (by mass) solution of benzoic acid ($C_6H_5CO_2H$) in benzene? Note: k_b for benzene is 2.53 ˚C·molal^{-1}.

Assume 100 g of solution;

$$\mathbf{12.5\ g\ C_6H_5CO_2H}\left(\frac{\mathbf{1\ mol}}{\mathbf{122\ g}}\right) = \mathbf{0.102\ mol\ C_6H_5CO_2H}$$

$$\mathbf{molality} = \frac{\mathbf{0.102\ mol\ C_6H_5CO_2H}}{\mathbf{0.0875\ kg\ C_6H_6}} = \mathbf{1.17\ molal}$$

$$\mathbf{\Delta T_{bp}} = \mathbf{mK_b}$$

$$= \mathbf{1.17molal}\left(\mathbf{2.53}\frac{\mathbf{^{\circ}\ C}}{\mathbf{molal}}\right)$$

$$\mathbf{\Delta T_{bp}} = \mathbf{2.95\ ^{\circ}C}$$

$$\mathbf{T_{bp}} = \mathbf{80.1 + 2.95\ ^{\circ}C = 83.0\ ^{\circ}C}$$

PS6.5. Given the following data;

Compound	(Experimental) ΔT_f of 1 mol of cmpd in 1 kg of H_2O	(Ideal) ΔT_f of 1 mol of cmpd in 1 kg of H_2O	Strong Weak or Nonelectrolyte
$C_6H_{12}O_6$	1.85 ˚C	**1.86 ˚C**	**Nonelectrolyte**
$(NH_2)_2CO$	1.87 ˚C	**1.86 ˚C**	**Nonelectrolyte**
NH_3	1.96 ˚C		**Weak electrolyte**
CH_3CO_2H	1.97 ˚C		**Weak electrolyte**
NaI	3.44 ˚C	**3.72 ˚C**	**Strong electrolyte**
KBr	3.50 ˚C	**3.72 ˚C**	**Strong electrolyte**
H_2SO_4	3.73 ˚C	**5.58 ˚C**	**Strong electrolyte**
K_2SO_4	5.40 ˚C	**5.58 ˚C**	**Strong electrolyte**

a) If each of the solutions is prepared by adding 1 mole of compound to 1 kg of water why does each have a different ΔT_f ?

The ΔT_f are different because substances behave differently when added to water. The freezing point depends on the number of particles in solution. Most covalent substances do not dissociate into ions when dissolved in water. Ionic substances dissociate into their constituent ions when dissolved in water. Generally ionic compounds produce larger ΔT_f, compared to covalent compounds (for the same molality of the solution) because of the higher number of particles in solution. An additional possibility is that some covalent substances partially dissociate into ions.

b) Determine the ideal ΔT_f for the above compounds, except NH_3 and CH_3CO_2H. Why can't we determine an ideal freezing point for NH_3 and CH_3CO_2H?

Based on the experimental data the freezing point 1 molal solutions of the covalent substances NH_3 and CH_3CO_2H behave differently compared the covalent substances $C_6H_{12}O_6$ and $(NH_2)_2CO$. For $C_6H_{12}O_6$ and $(NH_2)_2CO$ the freezing point data indicate both substances are behaving as non-electrolytes. The observed freezing points NH_3 and CH_3CO_2H however suggest there are more particles in solution than expected for a nonelectrolyte. A quick calculation to determine an experimental I yields,

$$\Delta T_{fp} = imK_f$$

$$1.96\ ˚C = i \cdot 1.00\ \text{molal}\left(1.86\frac{˚C}{m}\right)$$

$$i = 1.05$$

An i value of this magnitude indicates a small (5%) amount of the compound (NH_3 and CH_3CO_2H) dissociates into ions when dissolved in water. Weak electrolytes exhibit this type of behavior.

NaI and KBr are ionic compounds and dissociate when added to water according to the following equations

$$\mathbf{NaI}_{(aq)} \rightarrow \mathbf{Na}^+_{(aq)} + \mathbf{I}^-_{(aq)}$$

$$\mathbf{KBr}_{(aq)} \rightarrow \mathbf{K}^+_{(aq)} + \mathbf{Br}^-_{(aq)}$$

For each of these substances 1 mole of the compound produces 2 moles of particles.

PS6.5. (Continued)

$$\Delta T_f = 2.00 \text{ mol}\left(\frac{1.86^\circ\text{C}}{\text{molal}}\right) = 3.72\ ^\circ\text{C}$$

That both NaI and KBr have a smaller ΔT_f suggests that at the concentration of 1.00 molal some ionpairing is occurring to reduce the total number of particles in solution.

K_2SO_4 is an ionic compound and H_2SO_4 is a polar covalent compound. Both dissociate into ions when added to water according to the following equations

$$K_2SO_4(aq) \rightarrow 2K^+(aq) + SO_4^{2-}(aq)$$
$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

For each of these substances 1 mol dissolved in water produces 3 moles of particles.

$$\Delta T_f = 3.00 \text{ molal}\left(1.86\frac{^\circ\text{C}}{\text{m}}\right) = 5.58^\circ\text{C}$$

c) Why does the ideal ΔT_f differ from the experimental ΔT_f?

That each is less than the ideal suggests fewer particles are found experimentally in solution compared to the ideal number of particles. In the case of K_2SO_4, ion pairing at this high of a concentration (1 molal) lowers the ΔT_f slightly. In the case of H_2SO_4, the reaction written does not go to completion and fewer particles are produced. (We'll discuss H_2SO_4 in more detail later in the course.)

d) Classify each compound as a strong, weak or nonelectrolyte. (Place answers in the Table on Page 2.)

Classifying strong, weak and nonelectrolyte is done by looking at the experimental i values for each of the compounds. For sucrose and urea $i_{exp} = 1$ so they must be nonelectrolytes. For ammonia and acetic acid $i_{exp} = 1.05$ so they have a few ions in solution so they are weak electrolytes. For the remaining compounds i_{exp} is greater than 1 or 2 by quite a bit, so these must all be strong electrolytes

PS6.6. Determine the ideal freezing point of a solution prepared by mixing 2.52 g of $Ca(NO_3)_2$ in 300 g of water. The observed freezing point is –0.240 °C. Explain this difference.

$$2.52 \text{ g } Ca(NO_3)_2\left(\frac{1 \text{ mol}}{164 \text{ g}}\right) = 0.0154 \text{ mol } Ca(NO_3)_2$$

$$\text{molality} = \frac{0.0154 \text{ mol } Ca(NO_3)_2}{0.300 \text{ kg } H_2O} = 0.0513 \text{ molal}$$

$$\begin{aligned}\Delta T_{fp} &= imK_f \\ &= (3)0.0513 \text{ molal}\left(1.86\frac{^\circ\text{C}}{\text{molal}}\right) \\ \Delta T_{fp} &= 0.286\ ^\circ\text{C} \\ T_{fp} &= 0 - 0.286\ ^\circ\text{C} = -0.286\ ^\circ\text{C}\end{aligned}$$

The observed freezing point is higher (does not go as low as the ideal freezing point) suggesting that experimentally i is smaller than the ideal value of 3. This is likely when some ion-pairing exists in the solution. So some of the ions are closely associated with each other.

PS6.7. A 4.56 g sample of glycerol dissolved in 18.2 g of water elevated the boiling point by 1.38 ˚C.

a) What is the molar mass of glycerol?

From part b the composition of glycerol is carbon, hydrogen and oxygen. Most likely this substance is a non-electrolyte.

$$\Delta T_{bp} = imK_b \quad (\iota=1) \quad 1.38\ ^\circ C = m\left(0.512\frac{^\circ C}{m}\right)$$

$$m = \frac{1.38\ ^\circ C}{0.512\frac{^\circ C}{m}} = 2.70 \text{ molal}$$

$$\frac{2.70 \text{ mol glycerol}}{1 \text{ kg } H_2O} \times 0.0182 \text{ kg} = 0.0491 \text{ moles glycerol}$$

$$\frac{4.56 \text{ g glycerol}}{0.0491 \text{ mol glycerol}} = 92.8\ \frac{g}{mol}$$

b) Given the composition of glycerol is 39.1% C, 8.7% H and 52.2% O, by mass, what is its molecular formula?

$$39.1 \text{ g C}\left(\frac{1 \text{ mol C}}{12.0 \text{ g C}}\right) = 3.26 \text{ mol C}$$

$$8.7 \text{ g H}\left(\frac{1 \text{ mol H}}{1.01 \text{ g H}}\right) = 8.61 \text{ mol H}$$

$$52.2 \text{ g O}\left(\frac{1 \text{ mol O}}{16.00 \text{ g}}\right) = 3.26 \text{ mol O}$$

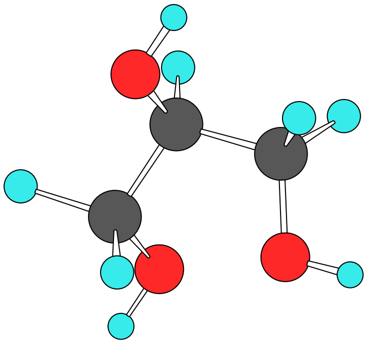
$$\left(\frac{3.26 \text{ mol C}}{3.26}\right) : \left(\frac{8.61 \text{ mol H}}{3.26}\right) : \left(\frac{3.26 \text{ mol O}}{3.26}\right)$$

1.0 C : 2.64 H : 1 O

3 · (1.0 C : 2.64 H : 1 O)

$C_3H_8O_3$

c) Suggest a possible Lewis structure for the glycerol molecule.



PS6.8. When 6.30 g of sulfur is dissolved in 450. g of diethyl ether the boiling point of ether is elevated by 0.115 ˚C. Note: k_b for ether is 2.10 ˚C·molal^{-1}.

a) What is the molar mass of sulfur dissolved in ether?

$$\Delta T_{bp} = imK_b \quad (i=1) \quad 0.115\ ^\circ C = m\left(2.10\frac{^\circ C}{m}\right)$$

$$m = \frac{0.115\ ^\circ C}{2.10\frac{^\circ C}{m}} = 0.0548 \text{ molal}$$

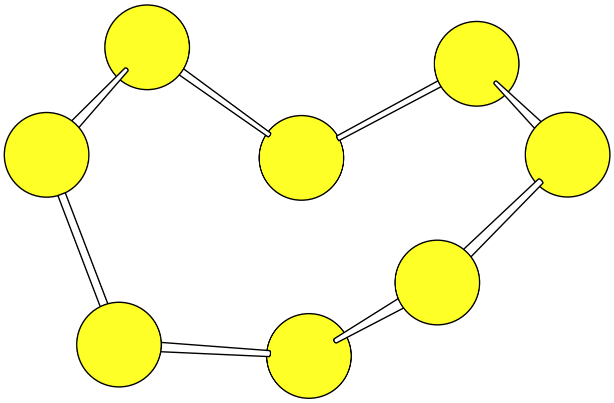
$$\frac{0.0548 \text{ mol sulfur}}{1 \text{ kg } CH_3CH_2OCH_2CH_3} \times 0.450 \text{ kg} = 0.0246 \text{ moles sulfur}$$

$$\frac{6.30 \text{ g sulfur}}{0.0246 \text{ mol sulfur}} = 256 \frac{g}{mol} \text{ sulfur}$$

$$256 \frac{g}{mol} \text{ sulfur} \left(\frac{1 \text{ mol S atoms}}{32 \text{ g}}\right) = 8.0 \text{ or 8 atoms per molecule.}$$

d) What is the molecular structure of sulfur in ether?

S_8 it is an eight-membered ring.



PS6.9. The freezing point depression of a 0.091 *m* solution of CsCl is 0.302 ˚C. The freezing point depression of a 0.091 *m* solution of $CaCl_2$ is 0.440 ˚C. In which solution does "ion-pairing" appear to be greater. Explain.

For CsCl:

$$\Delta T_{bp} = imK_b \qquad 0.302\ ^\circ C = i0.091\ m\left(1.86\frac{^\circ C}{m}\right)$$

$$i = \frac{0.302\ ^\circ C}{0.091\ m \cdot 1.86\frac{^\circ C}{m}} = 1.27$$

	$CsCl(aq) \rightarrow$	$Cs^+(aq)$ +	$Cl^-(aq)$
initial	**1**	**0**	**0**
change	**let x be the amount of the ionizes**		
	-x	**+x**	**+x**
final	**1 - x**	**x**	**x**

Total # particles = 1.27 = 1 - x + x + x

x = 0.27

Only 27% of the particles completely ionize.

PS6.9. (Continued)

For $CaCl_2$:

$$\Delta T_{bp} = imK_b \qquad 0.440\ ˚C = I\ 0.091\ m\left(1.86\frac{˚C}{m}\right)$$

$$i = \frac{0.440\ ˚C}{0.091\ m \cdot 1.86\frac{˚C}{m}} = 2.60$$

	$CaCl_2$ *(aq)* →	Ca^{2+}*(aq)* +	$2Cl^{-}$*(aq)*
initial	**1**	**0**	**0**
change	**let x be the amount of the ionizes**		
	-x	**+x**	**+2x**
final	**1 - x**	**x**	**2x**

Total # particles = 2.60 = 1 - x + x + 2x

x = 0.80

80% of the particles ionize.